

# PATENT SPECIFICATION

(11)

1 256 708

## DRAWINGS ATTACHED

- 1 256 708
- (21) Application No. 29882/71 (22) Filed 8 Nov. 1968
  - (62) Divided out of No. 1 256 707
  - (31) Convention Application Nos. 681 546 726 804 (32) Filed 8 Nov. 1967 6 May 1968 in
  - (33) United States of America (US)
  - (45) Complete Specification published 15 Dec. 1971
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  - (72) Inventors ROBERT P. OBRECHT  
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## (54) HYDROCHLORINATION OF METHANOL

PATENT RULES 1968

SPECIFICATION NO 1256708

The following amendment was made under Rule 94(3) on 3 May 1977:-

Page 1, Headings *delete* (31) Convention Application Nos 681546 726804 (32) Filed 8 Nov 1967. 6 May 1968 in (33) United States of America (US)

THE PATENT OFFICE  
20 May 1977

Bas 34549/11

Application here is disclosed an integrated process which comprises carrying out the  
20 vapour phase, thermal substitution chlorination of an alkane or an alkyl chloride containing one carbon atom in a first zone thereby producing a vapourous effluent comprising chlorine substituted materials in  
25 admixture with hydrogen chloride, said reaction in the first zone being carried out under substantially anhydrous conditions and under an elevated pressure above 5 pounds per square inch gauge withdrawing  
30 said effluent and passing same to a partial condensation zone to condense chlorine substituted materials while the substantially anhydrous hydrogen chloride remains gaseous, and passing said gaseous stream  
35 containing anhydrous hydrogen chloride without any substantial further purification as a feed material to a hydrogen chloride consuming reaction zone.

The invention therefore provides a process for reacting hydrogen chloride and methanol to form methyl chloride which comprises contacting methanol with a

by reference to the accompanying drawing which shows an integrated process including the partial chlorination of methyl chloride and the hydrochlorination of methanol.

Referring to the drawing, chlorine vapour in line 10, methyl chloride vapour in line 12 and/or vapourous recycle material containing methyl chloride in line 14 are intimately mixed and passed in line 16 to chlorination reactor 20. Chlorination reactor 20 is maintained under an elevated pressure of at least 5 psig. Suitable conditions are maintained in the chlorination reactor 20 to effect substitution chlorination of the methyl chloride to methylene chloride and/or chloroform, for example, substantially anhydrous conditions. Preferably the reaction is effected thermally in the absence of a catalyst at a temperature between 350 and 500°C.

The reaction effluent in line 22 contains unreacted  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ ,  $\text{CCl}_4$ , and by-product  $\text{HCl}$ . Gaseous material in line 22, at an elevated temperature and pressure,

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(72) Inventors ROBERT P. OBRECHT  
MARTIN J. BENNETT



## (54) HYDROCHLORINATION OF METHANOL

(71) We, STAUFFER CHEMICAL COMPANY, a corporation organised under the laws of the State of Delaware, United States of America, of 299 Park Avenue, New York, N.Y. 10017, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in

10 and by the following statement:—

This invention relates to a process for the hydrochlorination of methanol.

The process of this invention is particularly suitable for consuming the anhydrous hydrogen chloride produced by the process of our copending application No. 49076/68 (Serial No. 1 256 707). In that application there is disclosed an integrated process which comprises carrying out the vapour phase, thermal substitution chlorination of an alkane or an alkyl chloride containing one carbon atom in a first zone thereby producing a vapourous effluent comprising chlorine substituted materials in admixture with hydrogen chloride, said reaction in the first zone being carried out under substantially anhydrous conditions and under an elevated pressure above 5 pounds per square inch gauge withdrawing said effluent and passing same to a partial condensation zone to condense chlorine substituted materials while the substantially anhydrous hydrogen chloride remains gaseous, and passing said gaseous stream containing anhydrous hydrogen chloride without any substantial further purification as a feed material to a hydrogen chloride consuming reaction zone.

The invention therefore provides a process for reacting hydrogen chloride and methanol to form methyl chloride which comprises contacting methanol with a

stoichiometric excess of hydrogen chloride in a catalytic reaction zone at an elevated temperature and pressure to form methyl chloride, said catalytic zone containing an unmodified activated alumina or zinc chloride catalyst. It is usual to conduct the process in the vapour phase. The zinc chloride catalyst may be, either solid or a solution.

It is preferable to conduct the process at an elevated pressure of above 5 p.s.i.g. and our most preferred pressure is between 5 and 200 p.s.i.g.

The preferred molar ratio of methanol to hydrogen chloride is approximately 0.8:1.

The invention will be further illustrated by reference to the accompanying drawing which shows an integrated process including the partial chlorination of methyl chloride and the hydrochlorination of methanol.

Referring to the drawing, chlorine vapour in line 10, methyl chloride vapour in line 12 and/or vapourous recycle material containing methyl chloride in line 14 are intimately mixed and passed in line 16 to chlorination reactor 20. Chlorination reactor 20 is maintained under an elevated pressure of at least 5 psig. Suitable conditions are maintained in the chlorination reactor 20 to effect substitution chlorination of the methyl chloride to methylene chloride and/or chloroform, for example, substantially anhydrous conditions. Preferably the reaction is effected thermally in the absence of a catalyst at a temperature between 350 and 500°C.

The reaction effluent in line 22 contains unreacted  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ ,  $\text{CCl}_4$  and by-product  $\text{HCl}$ . Gaseous material in line 22, at an elevated temperature and pressure, 85

is introduced to quench tank 30 in which the effluent is contacted with relatively cool reflux material introduced from line 34. Quench column 30, is employed in the process to desuperheat the reactor effluent and to prevent solid by-product carryover from reaching the heat exchangers employed in the recovery system. Any suitable gas-liquid containing means, e.g., a multi-sieve plate column, can be employed in the operation of zone 30.

Substantially cooled vapour still under an elevated pressure, is withdrawn in line 38 and passed to a partial condensation zone, which in this process is represented by a series of condensers, 40, 42 and 44 and gas-liquid separators, 41, 43 and 45. It is to be understood that any suitable method and means for effecting partial condensation can be employed at this point in the process. In the preferred embodiment, condenser 40 employs water as the coolant material while condensers 42 and 44, operated at successively lower temperatures, employ suitable refrigerant cooling materials. The runoff from the gas-liquid separators is collected in storage tank 50. The liquid material withdrawn from tank 50 in line 52 is passed through a suitable drying trap, 54, and then split into two streams. A portion of the dried material is employed as reflux in line 34; and another portion is passed in line 56 to the product distillation purification system 60.

In the distillation purification system, crude chlorinated products, viz.,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ , and  $\text{CCl}_4$ , are separated in line 61 from unreacted methyl chloride which is recycled via line 62. When higher yields of chloroform are desired, methylene chloride is also recycled to the reactor for further chlorination.

Referring once again to the partial condensation zone, it is important that such partial condensation is carried out under elevated pressure conditions which will, of course, be slightly lower than the pressure in the chlorination zone. A suitable low temperature is maintained at terminal condenser 44. Substantially anhydrous conditions are maintained throughout the partial condensation zone such that the vapour stream issuing from separator 45 in line 66 comprises substantially anhydrous hydrogen chloride under an elevated pressure having a major part of the  $\text{CH}_2\text{Cl}_2$  and essentially all of the  $\text{CHCl}_3$  and  $\text{CCl}_4$  removed therefrom. In order to provide a suitable feed for a methanol hydrochlorination reactor, the exit conditions from the partial condensation zone are preferably maintained at a pressure between 50 and 200 psig and a temperature between  $-25^\circ$  and  $0^\circ\text{C}$ .

In the hydrochlorination reaction sub-

stantially anhydrous hydrogen chloride admixed with a small percentage of methyl chloride in line 66 is admixed with methanol vapour from line 68 and introduced to a suitable methanol hydrochlorination reactor 70 for the production of methyl chloride. The hydrochlorination reaction is effected in the presence of a catalyst, comprising solid unmodified activated alumina, or zinc chloride, either solid or in solution. Methanol hydrochlorination is well known, for example, see U.S. Patent No. 1,834,089 and French Patent No. 1,471,895. The hydrochlorination according to the invention is however carried out under superatmospheric pressure and using substantially pure hydrogen chloride in excess of the stoichiometric amount.

A vaporous effluent is recovered from zone 70 in line 72 comprising methyl chloride, hydrogen chloride and water. The effluent is then passed to a recovery system 74 which separates methyl chloride produced from the water of reaction. Water of reaction is removed and passed to waste containing small amounts of unreacted methyl alcohol, dimethyl ether, and unreacted or excess hydrogen chloride through line 75. Methyl chloride product and excess hydrogen chloride vapour saturated with water is withdrawn from the recovery system through line 82 and passed to drying zone 90. A preferable drying zone comprises a multiplate column irrigated counter currently with concentrated sulphuric acid. Concentrated sulphuric acid contacting also removes dimethyl ether impurities to a desired minimum level. The dried methyl chloride containing stream in line 91 is treated in a refrigerated condenser 92 to separate methyl chloride liquid in line 94. The desired amount of methyl chloride is fed through line 94 for utilization in chlorination reactor 20. Liquid methyl chloride (crude, technical grade) is withdrawn from line 94 and purified in a conventional manner to provide technical grade methyl chloride. Vaporous methyl chloride containing some hydrogen chloride, alternatively, can be removed from line 91 to a compressor (not shown) which then pumps the crude methyl chloride vapour directly to the chlorination reactor 20 vapour feed mixing inlet header. This alternative procedure avoids refrigeration duty in low temperature condenser 92 and subsequent reevaporation of the crude methyl chloride being recycled to the chlorination reactor 20. Substantially pure hydrogen chloride containing a small amount of methyl chloride is withdrawn in line 93 and can be further purified to yield a technically pure product.

It should also be pointed out that methyl chloride fed to reactor 20 can be added as

a highly atomized liquid spray thereby permitting operating with higher chlorine to methyl chloride ratio in the single reactor system. The methyl chloride can also be introduced as a highly atomized liquid spray to both reactors of a two-series reactor system. When a higher yield of chloroform is desired, methylene chloride and methyl chloride are recycled to one or more reactors. For maximum thermodynamic economy, both the methylene chloride and the methyl chloride recycle are introduced to the reactor inlet or inlets as a highly atomized liquid spray, for example as described in U.S. Patent No. 3,126,419.

The following example illustrates the invention:—

#### Example 1

The following feed materials are intimately admixed and passed in line 16 to thermal chlorination reactor 20: 87.47 lb. mols per hr. of superheated chlorine vapour at 25°C; 68.63 lb. mols per hr. methyl chloride vapour and 255.7 lb. mols per hr. recycle streams consisting of 186.4 lb. mols per hr. methyl chloride, 41.02 lb. mols per hr. hydrogen chloride, and 28.3 lb. mols per hr. methylene chloride. Reactor 20 is maintained at an operating pressure of 110 psig and the maximum temperature attained in the reactor is 425°C. Reaction takes place in the reactor which provides a retention time of 12 seconds. No free or unreacted chlorine is found in the reactor exit gas which is flowed to quench column 30. A liquid stream collected in tank 50 is introduced to quench tank 30 via line 34 in an upper portion thereof. The temperature at the bottom of quench vessel 30 is maintained at 120°C while the effluent vapour at the top of quench vessel 30 is at a temperature of 100°C. Indirect water cooling is effected in condenser 40 to cool the vaporous material in line 38 to a temperature of 40°C. Refrigerant cooling is effected to achieve a temperature of 10°C in condenser 42 and a temperature of -12°C in condenser 44. The terminal pressure of the gaseous material at the exit end of condenser 44 is 100 psig.

The uncondensed material in line 66 has the following flow composition: 90.39 lb. mols per hr. hydrogen chloride; 13.56 lb. mols per hr. methyl chloride; and 0.01 lb. mols per hr. methylene chloride. Material in line 66 is admixed with 72.24 lb. mols per hr. of superheated methanol. The combined vapour is then fed to methanol hydrochlorination reactor 70 containing an unmodified activated alumina catalyst. Reaction heat is removed by a boiling heat transfer fluid contained in the jacketed side of reactor 70. In this example, the reaction effluent is reduced in temperature

by passing through a conventional heat exchange recovery system 74. All of the water of reaction is removed from the process as 22 wt% hydrochloric acid via line 75. The methyl chloride product, plus any excess hydrogen chloride vapor, saturated with water, is dried in multi plate drying column 90 which is counter currently irrigated with concentrated sulphuric acid. The dried methyl chloride-hydrogen chloride containing stream is passed to a low temperature condenser 92 in which methyl chloride is condensed and fed to the partial chlorination process in line 94. Any non-condensable hydrogen chloride present is withdrawn in line 93.

When maximum methylene chloride production is desirable, a low chloride ratio and a single chlorinated reactor, e.g., 20, is preferably employed with the excess methyl chloride acting as a diluent to control reaction temperature. When it is desirable to maximize the chloroform to methyl chloride product ratio via methyl chloride substitution chlorination, two reaction zones arranged in series can be employed as shown in U.S. Patent No. 3,126,419.

#### WHAT WE CLAIM IS:—

1. A process for reacting hydrogen chloride and methanol to form methyl chloride which comprises contacting methanol with a stoichiometric excess of hydrogen chloride in a catalytic reaction zone at an elevated temperature and pressure to form methyl chloride, said catalytic zone containing an unmodified activated alumina or zinc chloride catalyst.

2. A process as claimed in claim 1 in which the reaction is conducted in the vapour phase.

3. A process as claimed in claim 1 or claim 2 which comprises contacting methanol with a stoichiometric excess of hydrogen chloride in a reactor at an elevated pressure above 5 psig in the presence of an unmodified activated alumina catalyst, said reactor being cooled by boiling heat transfer fluid in the jacketed side of the vessel, cooling the reactor effluent and separating the condensate containing water from the gaseous phase containing methyl chloride, contacting the gaseous phase containing methyl chloride with sulphuric acid to recover a dry gaseous phase containing methyl chloride.

4. A process as claimed in any of claims 1 to 3 in which the elevated pressure is between 5 and 200 pounds per square inch gauge.

5. A process as claimed in any of claims 1 to 4 in which the molar ratio of methanol to hydrogen chloride is about 0.8:1.

6. A process as claimed in claim 1 substantially as herein described with reference

to the Example.

7. Methyl chloride when prepared by a process as claimed in any of claims 1 to 6.

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